Category

Polymer-Supported Synthesis

Key words

iron nanoparticles

cyclopropanation

diazoesters

alkenes

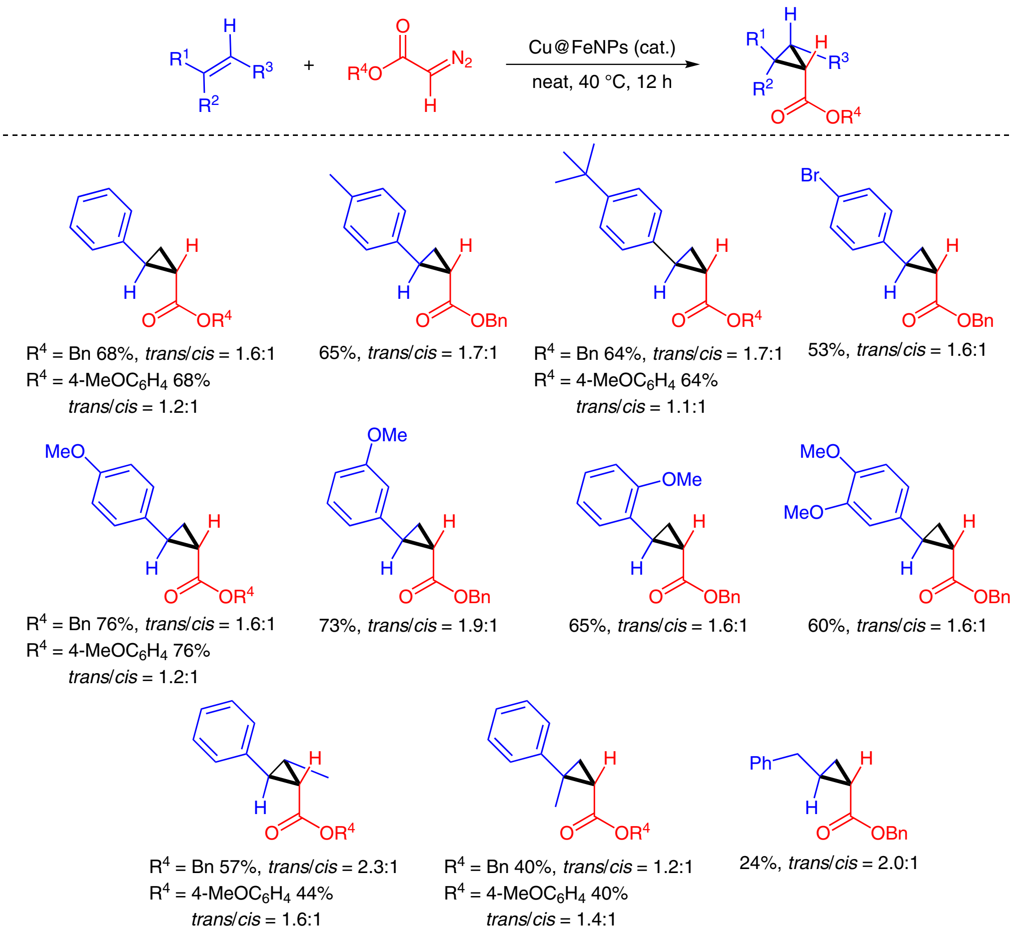
copper

S. ISHIKAWA, R. HUDSON, M. MASNADI, M. BATEMAN, A. CASTONGUAY, N. BRAIDY, A. MOORES,* C.-J. LI* (MCGILL UNIVERSITY, MONTREAL AND UNIVERSITÉ DE SHERBROOKE, CANADA)

Cyclopropanation of Diazoesters with Styrene Derivatives Catalyzed by Magnetically Recoverable Copper-Plated Iron Nanoparticles

Tetrahedron **2014**, *70*, 8952–8958.

Cyclopropanation of Alkenes with Diazoesters Using Cu@FeNPs



R^4 = Bn 68%, *trans*/*cis* = 1.6:1
R^4 = 4-$MeOC_6H_4$ 68%
trans/*cis* = 1.2:1

65%, *trans*/*cis* = 1.7:1

R^4 = Bn 64%, *trans*/*cis* = 1.7:1
R^4 = 4-$MeOC_6H_4$ 64%
trans/*cis* = 1.1:1

53%, *trans*/*cis* = 1.6:1

R^4 = Bn 76%, *trans*/*cis* = 1.6:1
R^4 = 4-$MeOC_6H_4$ 76%
trans/*cis* = 1.2:1

73%, *trans*/*cis* = 1.9:1

65%, *trans*/*cis* = 1.6:1

60%, *trans*/*cis* = 1.6:1

R^4 = Bn 57%, *trans*/*cis* = 2.3:1
R^4 = 4-$MeOC_6H_4$ 44%
trans/*cis* = 1.6:1

R^4 = Bn 40%, *trans*/*cis* = 1.2:1
R^4 = 4-$MeOC_6H_4$ 40%
trans/*cis* = 1.4:1

24%, *trans*/*cis* = 2.0:1

Significance: Copper-plated iron nanoparticles (Cu@FeNPs) catalyzed the cyclopropanation of alkenes with diazoesters to give the corresponding substituted cyclopropanes in up to 76% yield (16 examples). In the reaction of 4-vinylanisole with benzyl diazoacetate, the catalyst was recovered by magnetic separation and reused four times without significant loss of catalytic activity.

Comment: The authors reported previously the preparation of Cu@FeNPs and its application to the Huisgen reaction (*Green Chem.* **2012**, *14*, 622). ICP analysis revealed that 12 ppm of copper leached out from the fresh catalyst during the reaction. The leached copper species showed no catalytic activity.

SYNFACTS Contributors: Yasuhiro Uozumi, Hiroaki Tsuji
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Category

Polymer-Supported Synthesis

Key words

nanoporous gold

reduction

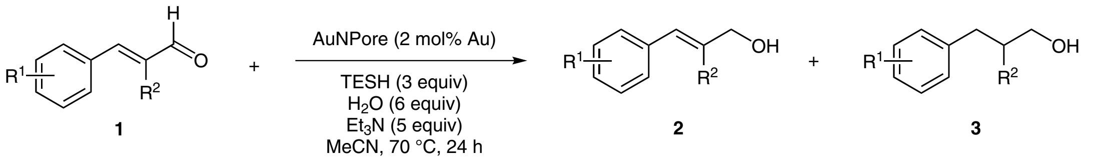
α,β-unsaturated aldehydes

alcohols

B. S. TAKALE, S. WANG, X. ZHANG, X. FENG, X. YU, T. JIN, M. BAO,* Y. YAMAMOTO*
(DALIAN UNIVERSITY OF TECHNOLOGY, P. R. OF CHINA AND TOHOKU UNIVERSITY, SENDAI, JAPAN)

Chemoselective Reduction of α,β-Unsaturated Aldehydes Using An Unsupported Nanoporous Gold Catalyst
Chem. Commun. **2014**, *50*, 14401–14404.

Chemoselective Reduction of α,β-Unsaturated Aldehydes with AuNPore



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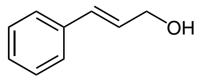
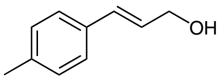
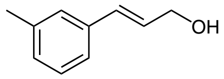
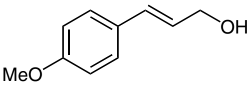
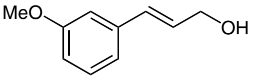

73% yield, **2**/**3** > 99:1


70% yield, **2**/**3** = 100:0

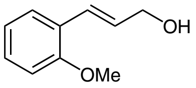

71% yield, **2**/**3** = 89:11



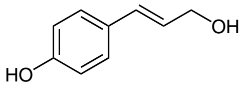
78% yield, **2**/**3** = 91:9



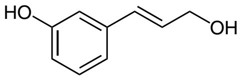
70% yield, **2**/**3** = 91:9



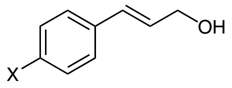
70% yield, **2**/**3** = 82:18



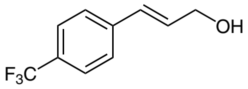
75% yield, **2**/**3** = 100:0



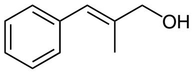
70% yield, **2**/**3** > 99:1

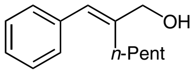


X = Br, 45% yield, **2**/**3** = 100:0
X = F, 42% yield, **2**/**3** = 100:0



46% yield, **2**/**3** > 99:1


69% yield, **2**/**3** > 99:1



62% yield, **2**/**3** = 97:3

Significance: Nanoporous gold (AuNPore) catalyzed the 1,2-reduction of α,β-unsaturated aldehydes **1** with triethylsilane. The reduction was carried out in the presence of water and triethylamine to give the corresponding allyl alcohols **2** in 42–78% yield with 82:18 to 100:0 (**2**/**3**) chemoselectivity.

Comment: Previously, the authors reported the AuNPore-catalyzed chemoselective reduction of imines with dimethylphenylsilane (*Org. Lett.* **2014**, *16*, 2558). In the reduction of cinnamyl aldehyde, the catalytic activity of AuNPore was superior to that of $Au_{30}Ag_{70}$ alloy, homogeneous AuCl(Ph$_3$P)/Bu$_3$P, and AuCl/IPr·HCl. ICP-MS analysis showed that no gold content was leached from the catalyst during the reaction.

SYNFACTS Contributors: Yasuhiro Uozumi, Fumie Sakurai
Synfacts 2015, 11(1), 0098 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379712; **Reg-No.:** Y14214SF

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Hollow Zeolitic Imidazolate Framework Nanospheres as Highly Efficient Cooperative Catalysts for [3+3] Cycloaddition Reactions
J. Am. Chem. Soc. **2014**, *136*, 13963–13966.

Category

Polymer-Supported Synthesis

Key words

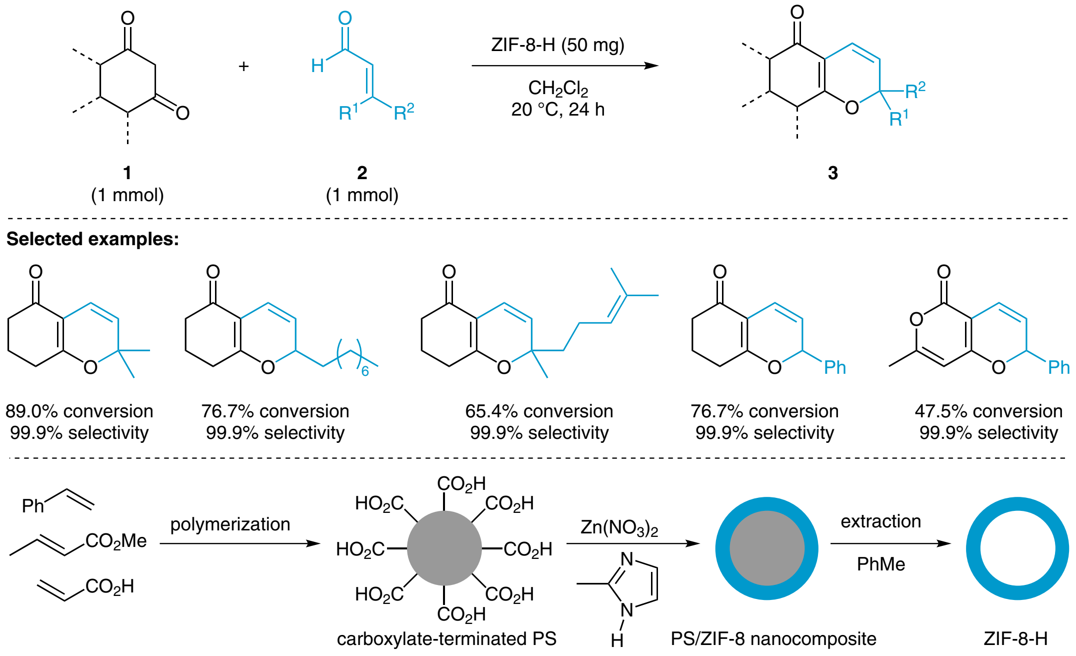
zeolitic imidazolate framework

hollow-structured nanospheres

[3+3] cycloaddition

zinc

A Zeolitic Imidazolate Framework Catalyst for [3+3] Cycloadditions



Significance: The authors developed a hollow-structured zeolitic imidazolate framework (ZIF-8-H) nanosphere as a catalyst for [3+3] cycloadditions. ZIF-8-H was prepared via complexation of carboxylic groups on the surface of nano-PS (ø = 400 nm) with zinc ions and 2-methylimidazole, followed by subsequent removal of the PS nanosphere by extraction with toluene. The reaction of 1,3-dicarbonyl compounds **1** with α,β-unsaturated aldehydes **2** proceeded in the presence of ZIF-8-H to give the pyranyl heterocycles **3** with up to 89.0% conversion and 99.9% selectivity.

Comment: The reaction of 1,3-hexanedione and 3-methyl-2-butenal proceeded in the presence of ZIF-8-H with 89.0% conversion, whereas the use of bulk ZIF-8 showed lower catalytic efficiency (73.2% conversion). Toluene vapor adsorption isotherm showed that ZIF-8-H absorbed toluene to a cage-filling level with a high adsorption amount (6.34 mmol/g). Based on this observation, the authors discussed that the limiting aperture size of ZIF-8-H exceeded the kinetic diameter of toluene (0.61 nm), which is much larger than the reported window size of ZIF-8 (0.34 nm).

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato
Synfacts 2015, 11(1), 0099 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379726; **Reg-No.:** Y15314SF

Category

Polymer-Supported Synthesis

Key words

cobalt oxide

magnetite

hydroacylation

azodicarboxylates

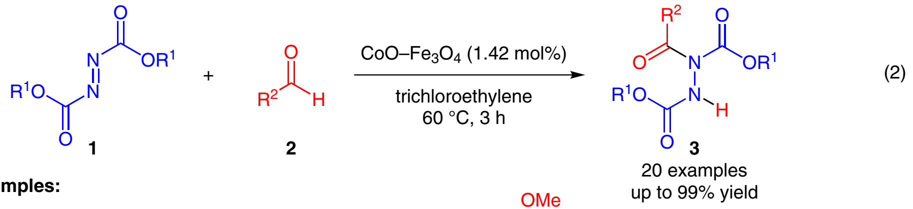
J. M. PÉREZ, D. J. RAMÓN* (UNIVERSIDAD DE ALICANTE, SPAIN)

Cobalt-Impregnated Magnetite as General Heterogeneous Catalyst for the Hydroacylation Reaction of Azodicarboxylates

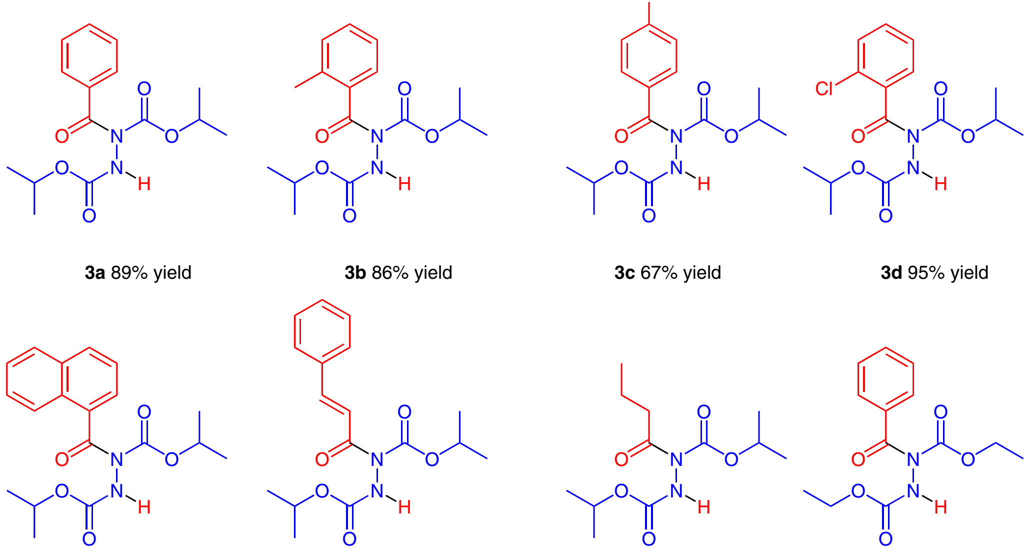
Adv. Synth. Catal. **2014**, *356*, 3039–3047.

Hydroacylation of Azodicarboxylates with Aldehydes Using $CoO–Fe_3O_4$

$$CoCl_2\cdot 6H_2O \xrightarrow[H_2O]{Fe_3O_4} \xrightarrow{NaOH} \xrightarrow[100\ °C,\ 24\ h]{} CoO–Fe_3O_4 \qquad (1)$$



Selected examples:



3a 89% yield

3b 86% yield

3c 67% yield

3d 95% yield

3e 87% yield

3f 74% yield

3g 99% yield

3h 99% yield

Significance: Magnetite-supported cobalt oxide ($CoO–Fe_3O_4$) was prepared by mixing $CoCl_2\cdot 6H_2O$ and Fe_3O_4 in water followed by treatment with NaOH (eq. 1). $CoO–Fe_3O_4$ catalyzed the hydroacylation of azodicarboxylates **1** with aldehydes **2** in trichloroethylene to afford the hydroacylated products **3** in up to 99% yield (eq. 2).

Comment: In the formation of **3a**, the catalyst was recovered by magnetic separation and reused nine times with slight loss of its catalytic activity. The catalytic activity of $CoO–Fe_3O_4$ was superior to that of the other metal oxides supported on Fe_3O_4 ($NiO–Fe_3O_4$, $CuO–Fe_3O_4$, $Ru_2O_3–Fe_3O_4$, $Rh_2O_3–Fe_3O_4$, $PdO–Fe_3O_4$, $Ag_2O/Ag–Fe_3O_4$, $WO_x–Fe_3O_4$, $OsO–Fe_3O_4$, $PtO/PtO_2–Fe_3O_4$, $Au_2O_3/Au–Fe_3O_4$, $NiO/Cu–Fe_3O_4$, $PdO/Cu–Fe_3O_4$) and unsupported CoO.

SYNFACTS Contributors: Yasuhiro Uozumi, Noboru Kobayashi
Synfacts 2015, 11(1), 0100 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379716; **Reg-No.:** Y14614SF

J. MALMGREN, A. NAGENDIRAN, C.-W. TAI, J. E. BÄCKVALL,* B. OLOFSSON*
(STOCKHOLM UNIVERSITY, SWEDEN)
C2-Selective Arylation of Indoles with Heterogeneous Nanopalladium and Diaryliodonium Salts
Chem. Eur. J. **2014**, *20*, 13531–13535.

Category

Polymer-Supported Synthesis

Key words

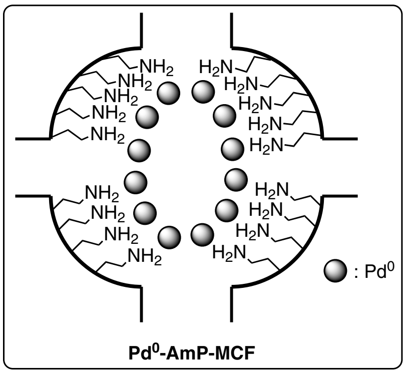
arylation

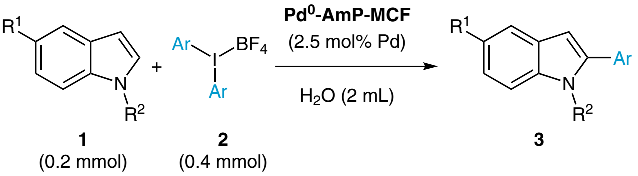
diaryliodonium salts

indoles

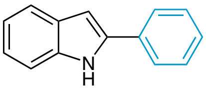
palladium catalysis

A Heterogeneous Palladium Catalyst for C2-Selective Arylation of Indoles

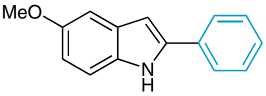




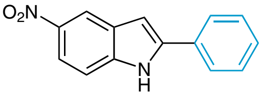
Selected results:



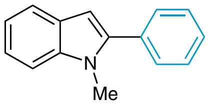
3a
R^1 = H, R^2 = H, Ar = Ph
r.t., 6 h, 91% yield



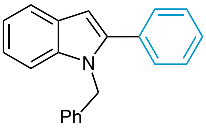
3b
R^1 = MeO, R^2 = H, Ar = Ph
40 °C, 6 h, 86% yield



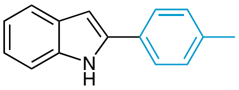
3c
R^1 = NO_2, R^2 = H, Ar = Ph
50 °C, 25 h, 70% yield



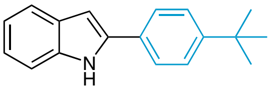
3d
R^1 = H, R^2 = Me, Ar = Ph
r.t., 6 h, 80% yield



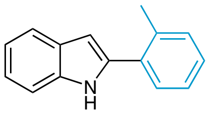
3e
R^1 = H, R^2 = MeC_6H_5, Ar = Ph
50 °C, 24 h, 65% yield



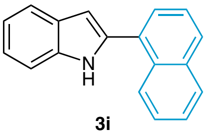
3f
R^1 = H, R^2 = H, Ar = 4-MeC_6H_4
40 °C, 6 h, 83% yield



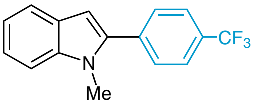
3g
R^1 = H, R^2 = H, Ar = 4-*t*-BuC_6H_4
r.t., 15 h, 84% yield



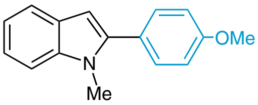
3h
R^1 = H, R^2 = H, Ar = 2-MeC_6H_4
40 °C, 6 h, 76% yield



3i
R^1 = H, R^2 = H, Ar = Np
40 °C, 15 h, 67% yield



3j
R^1 = H, R^2 = Me, Ar = 4-$F_3CC_6H_4$
40 °C, 15 h, 99% yield



3k
R^1 = H, R^2 = Me, Ar = 4-$MeOC_6H_4$
40 °C, 6 h, 72% yield

Significance: Pd^0-AmP-MCF constitutes of silica-based mesocellular foam (MCF) functionalized with aminopropylsilane (for the preparation, see: M. Shakeri et al. *Chem. Eur. J.* **2011**, *17*, 13269). Pd^0-AmP-MCF (palladium particles ø: 2–3 nm) catalyzed the C2-selective arylation of indoles **1** and substituted diaryliodonium tetrafluoroborates **2** to give the corresponding indole derivatives in 65–99% yield (15 examples).

Comment: The reactions of an electron-rich indole (**3b**), an N-methylated indole (**3d**), *para*-alkyl-substituted salts (**3f**,**g**), or an electron-deficient CF_3-substituted salt (**3j**) afforded high yields, whereas an N-benzylated indole (**3e**) or a naphthyl salt (**3i**) resulted in lower yield. ICP-OES analysis showed 0.6 ppm of palladium leaching from the reaction mixture (**3a**).

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Rikako Ishii
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DOI: 10.1055/s-0034-1379722; **Reg-No.:** Y14914SF

Category

Polymer-Supported Synthesis

Key words

borylation

cyclopropanes

cyclobutanes

silica gel supported phosphines

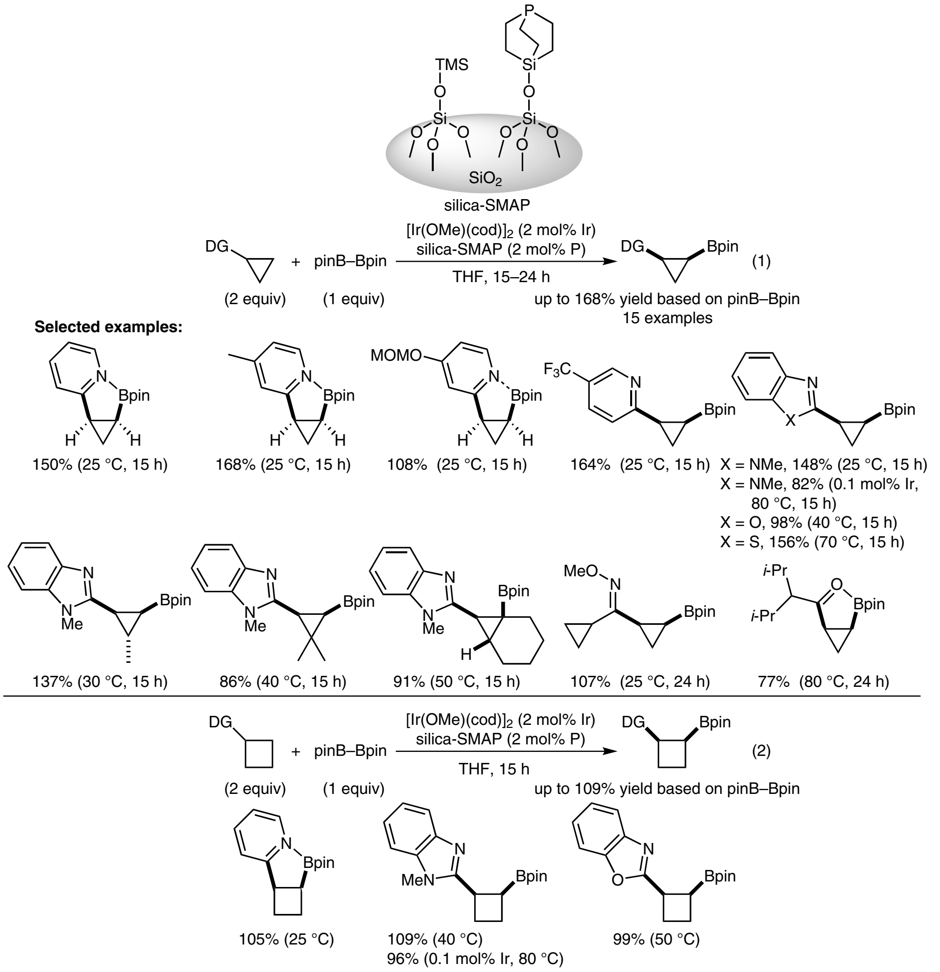
iridium

R. MURAKAMI, K. TSUNODA, T. IWAI, M. SAWAMURA* (HOKKAIDO UNIVERSITY, SAPPORO, JAPAN)

Stereoselective C–H Borylations of Cyclopropanes and Cyclobutanes with Silica-Supported Monophosphane–Ir Catalysts

Chem. Eur. J. **2014**, *20*, 13127–13131.

C–H Borylation of Cyclopropanes and Cyclobutanes with Silica-SMAP–Iridium



Significance: The heteroatom-directed C–H borylation of cyclopropanes and cyclobutanes with bis(pinacolato)diboron was carried out in the presence of $[Ir(OMe)(cod)]_2$ and silica-SMAP to give the corresponding borylated products in up to 168% yield based on bis(pinacolato)diboron (eqs. 1 and 2).

Comment: In the reaction of 2-cyclopropylpyridine with bis(pinacolato)diboron, the catalytic activity of the silica-SMAP–iridium system was superior to that of the other ligand–iridium systems (for example, 0% yield for Ph-SMAP–Ir, Me_3P–Ir, *t*-Bu_3P–Ir, Ph_3P–Ir, XPhos–Ir, dtbpy–Ir, and 2,9-Me_2Phen–Ir).

SYNFACTS Contributors: Yasuhiro Uozumi, Go Hamasaka
Synfacts 2015, 11(1), 0102 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379710; **Reg-No.:** Y14014SF

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Supported Ruthenium–Carbene Catalyst on Ionic Magnetic Nanoparticles for Olefin Metathesis
Org. Lett. **2014**, *16*, 4969–4971.

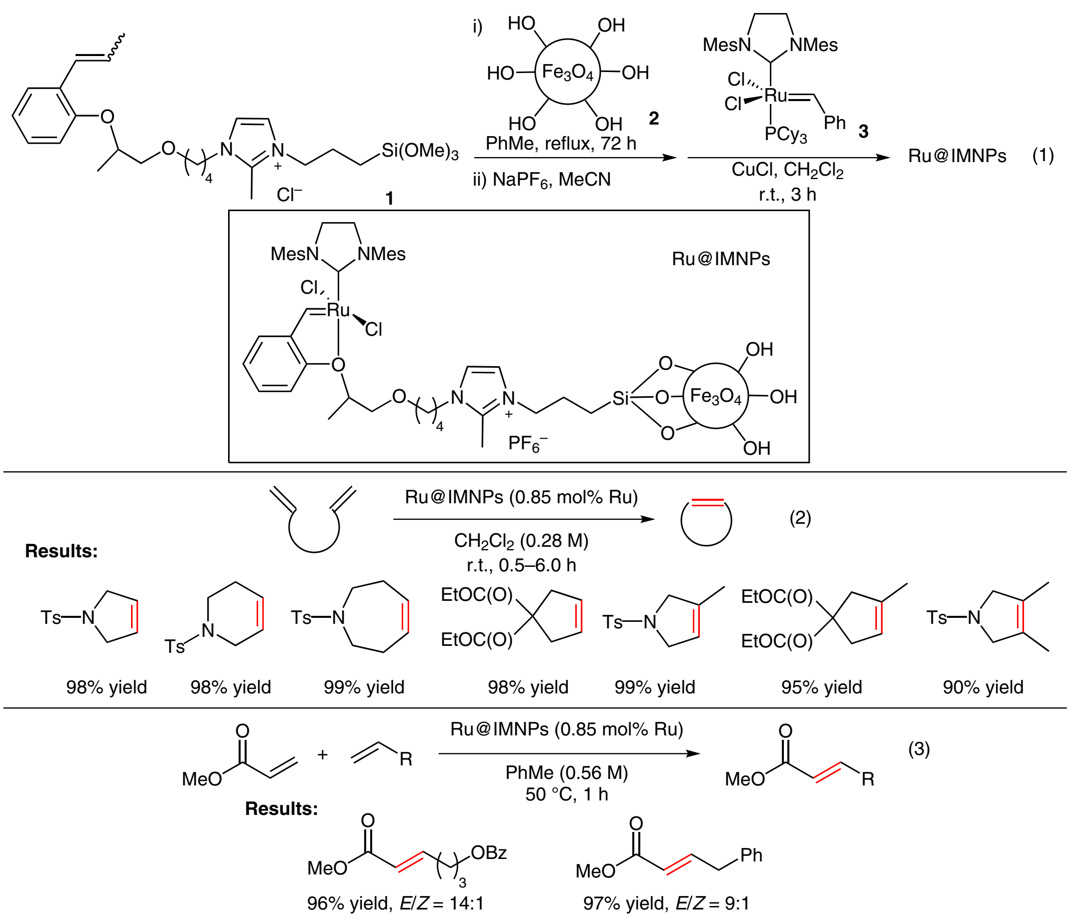
Category

Polymer-Supported Synthesis

Key words

carbenes
iron oxide
olefin metathesis
ruthenium

Olefin Metathesis with Ruthenium–Carbene Supported on Iron Oxide



Significance: The Grubbs–Hoveyda ruthenium–carbene complex supported on ionic magnetic nanoparticles (Ru@IMNPs) was prepared by immobilization of imidazolium chloride **1** onto Fe_3O_4 **2**, anion exchange with $NaPF_6$, and metathesis with ruthenium complex **3** (eq. 1). Ru@IMNPs catalyzed the ring-closing metathesis of dienes to give the corresponding cyclic olefins in 90–99% yield (eq. 2). The cross-metathesis of methyl acrylate with olefins using Ru@IMNPs also proceeded with high *E*-selectivity (eq. 3).

Comment: In the ring-closing metathesis of *N*,*N*-diallyl tosylamide, the catalyst was recovered magnetically and reused five times without significant loss of catalytic activity (6th run: 96% conversion), although ICP-MS analysis showed significant leaching of the ruthenium species into the product (a loss of 54% of the ruthenium content of the fresh catalyst) during the initial three runs of the recycling experiment.

SYNFACTS Contributors: Yasuhiro Uozumi, Takao Osako
Synfacts 2015, 11(1), 0103
DOI: 10.1055/s-0034-1379713; **Reg-No.:** Y14314SF

Category

Polymer-Supported Synthesis

Key words

triazoles

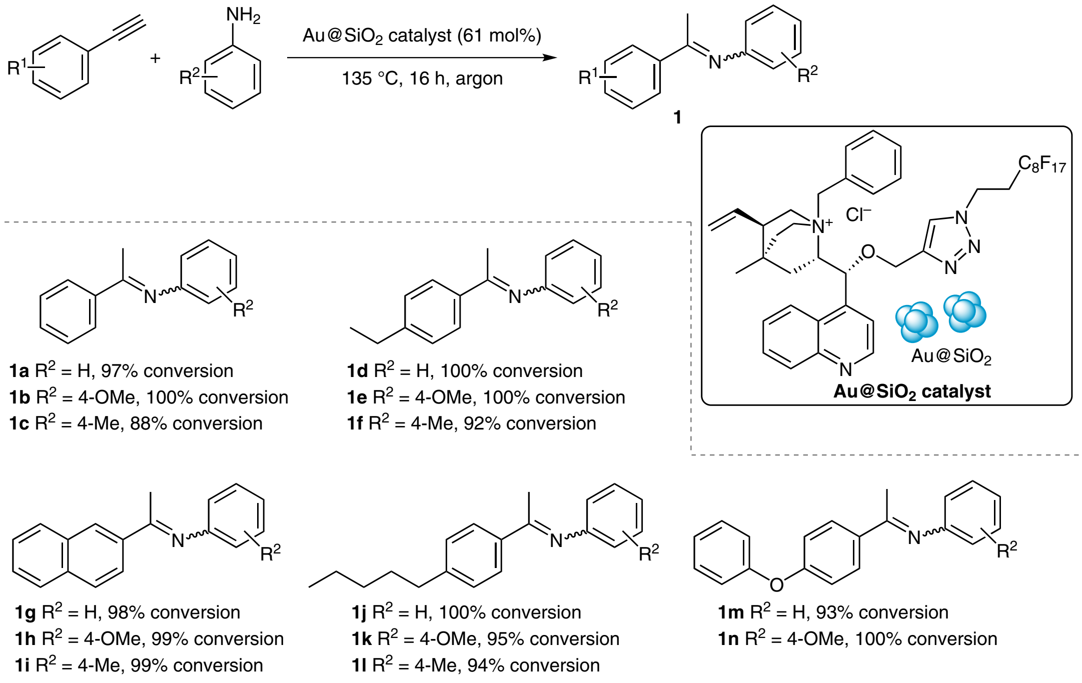
hydroamination

gold nanoparticles

heterogeneous catalysis

V. A. SOLOVYEVA, K. B. VU, Z. MERICAN, R. SOUGRAT, V. O. RODIONOV* (KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, THUWAL, KINGDOM OF SAUDI ARABIA)
One-Pot Synthesis of Au@SiO$_2$ Catalysts: A Click Chemistry Approach
ACS Comb. Sci. **2014**, *16*, 513–517.

Hydroamination of Alkynes Using Amphiphiles-Based Au@SiO$_2$



1a R^2 = H, 97% conversion
1b R^2 = 4-OMe, 100% conversion
1c R^2 = 4-Me, 88% conversion

1d R^2 = H, 100% conversion
1e R^2 = 4-OMe, 100% conversion
1f R^2 = 4-Me, 92% conversion

1g R^2 = H, 98% conversion
1h R^2 = 4-OMe, 99% conversion
1i R^2 = 4-Me, 99% conversion

1j R^2 = H, 100% conversion
1k R^2 = 4-OMe, 95% conversion
1l R^2 = 4-Me, 94% conversion

1m R^2 = H, 93% conversion
1n R^2 = 4-OMe, 100% conversion

Significance: The porous Au@SiO$_2$ catalyst was prepared from a gold precursor and a TEOS solution in the presence of cinchonidine-based triazole amphiphiles. The hydroamination of alkynes was carried out with Au@SiO$_2$ to give the corresponding imine products **1a**–**n** in up to 99% conversion.

Comment: The turnover number of Au@SiO$_2$ was 1604 for the formation of **1b**. The catalyst was characterized by cryo-TEM, XPS, UV/Vis, zeta potential, and ICP-OES analyses.

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek
Synfacts 2015, 11(1), 0104 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379718; **Reg-No.:** Y14814SF

H. ZHAO, W. HE, R. YAO, M. CAI* (JIANGXI NORMAL UNIVERSITY, NANCHANG AND GUANGDONG PHARMACEUTICAL UNIVERSITY, GUANGZHOU, P. R. OF CHINA)
Heterogeneous Copper-Catalyzed Cascade Three-Component Reaction of Amines, Carbon Disulfide and 2-Iodoanilines Leading to 2-Aminobenzothiazoles
Adv. Synth. Catal. **2014**, *356*, 3092–3098.

Category

Polymer-Supported Synthesis

Key words

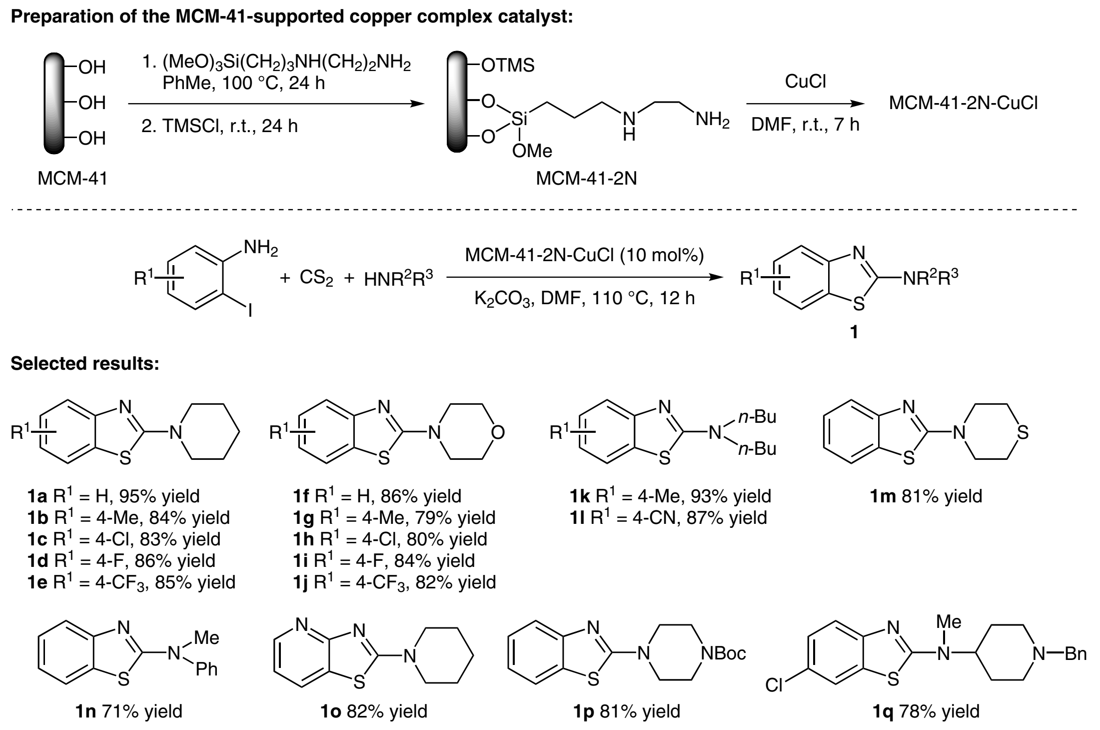
MCM-41

2-aminobenzothiazoles

copper complexes

heterogeneous catalysis

Preparation of 2-Aminobenzothiazoles with an MCM-41-Cu Catalyst



Significance: The mesoporous catalyst MCM-41-2N-CuCl was prepared by immobilization of a 3-(2-aminoethylamino)propyl moiety on MCM-41 with CuCl. The reaction of 2-iodoanilines, carbon disulfide (CS_2) and amines with 10 mol% of MCM-41-2N-CuCl gave the corresponding 2-aminobenzothiazoles **1a**–**q** in up to 95% yield.

Comment: The MCM-41-2N-CuCl catalyst was recovered by filtration and reused nine times to give **1a** (5th reuse: 94% yield, 9th reuse: 93% yield). ICP-AES analysis revealed that no copper species leached into the reaction mixture.

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Heeyoel Baek
Synfacts 2015, 11(1), 0105
DOI: 10.1055/s-0034-1379717; **Reg-No.:** Y14714SF

Category

Polymer-Supported Synthesis

Key words

1,2,3-triazoles

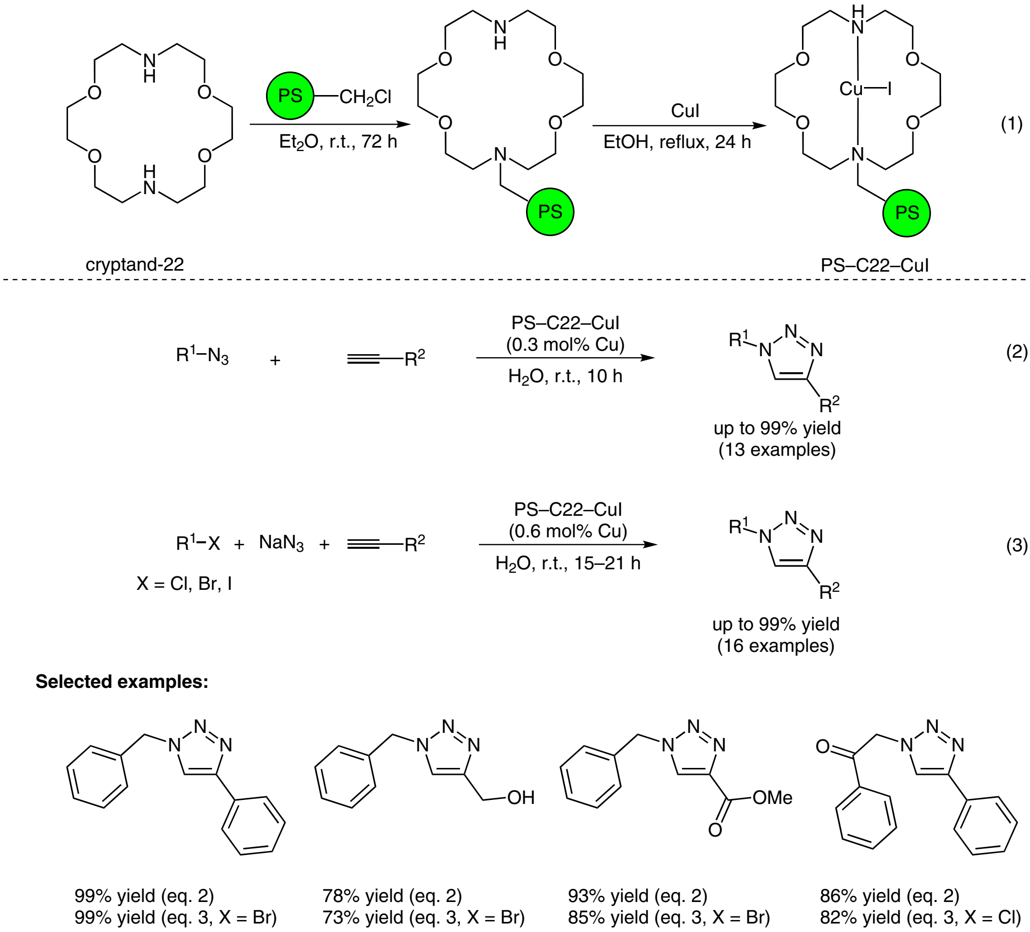
sodium azide

terminal alkynes

polystyrene resin

B. MOVASSAGH,* N. REZAEI (K. N. TOOSI UNIVERSITY OF TECHNOLOGY, TEHRAN, IRAN)
Polystyrene Resin-Supported CuI–Cryptand-22 Complex: A Highly Efficient and Reusable Catalyst for Three-Component Synthesis of 1,4-Disubstituted 1,2,3-Triazoles Under Aerobic Conditions in Water
Tetrahedron **2014**, *70*, 8885–8892.

Click Reaction Using Polymer-Supported CuI–Cryptand-22



Significance: A polystyrene resin supported CuI–cryptand-22 complex (PS–C22–CuI) was prepared by mixing chloromethylated polystyrene with cryptand-22 in diethyl ether, followed by the complexation with CuI in ethanol (eq. 1). PS–C22–CuI catalyzed the click reaction of azides with terminal alkynes (eq. 2, method A) or the one-pot three-component reaction from alkyl halides, sodium azide, and terminal alkynes (eq. 3, method B) to give the corresponding 1,2,3-triazoles in up to 99% yield.

Comment: The PS–C22–CuI complex was characterized by FT-IR, EDX, SEM, XPS, and TG-DTA analysis. In both methods A and B for synthesizing 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, the catalyst was recovered by filtration and reused three times.

SYNFACTS Contributors: Yasuhiro Uozumi, Shiguang Pan
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A. Z. WILCZEWSKA,* I. MISZTALEWSKA (UNIVERSITY OF BIALYSTOK, POLAND)
Direct Synthesis of Imidazolinium Salt on Magnetic Nanoparticles and Its Palladium Complex Application in the Heck Reaction
Organometallics **2014**, *33*, 5203–5208.

The Mizoroki–Heck Reaction Using a Palladium–NHC Complex Supported on MNP

Category

Polymer-Supported Synthesis

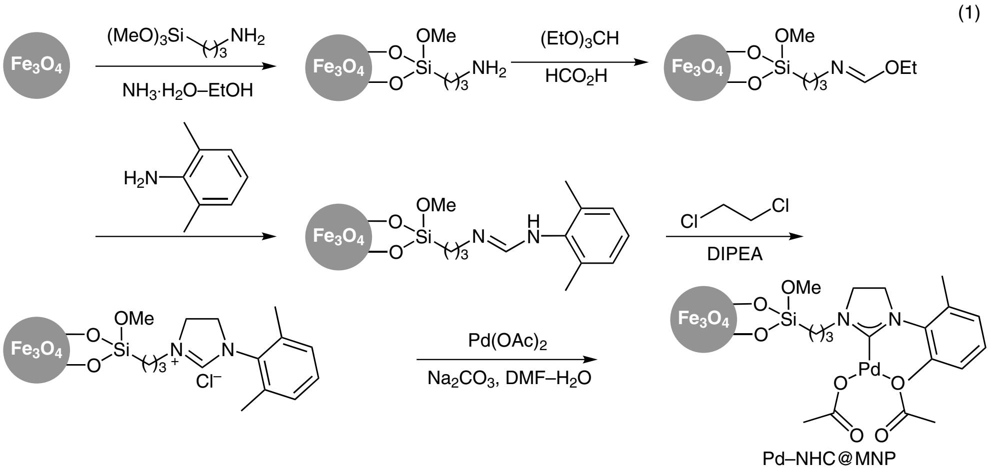
Key words

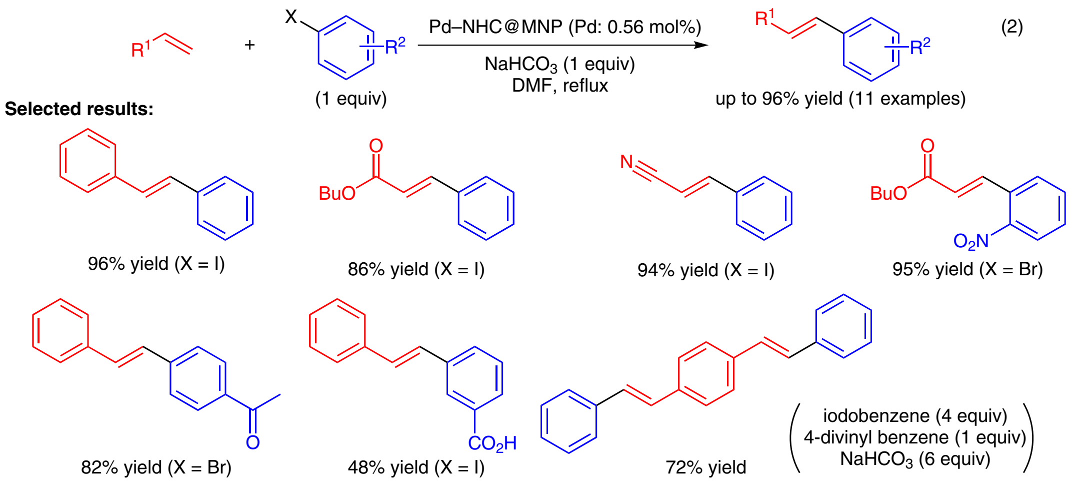
N-heterocyclic carbenes

magnetic nanoparticles

Mizoroki–Heck reaction

palladium





Significance: A palladium–NHC complex was immobilized on magnetic nanoparticles (Pd–NHC@MNP) according to the sequences shown above. Pd–NHC@MNP catalyzed the Mizoroki–Heck reaction of terminal alkenes with aryl halides to afford the corresponding internal alkenes in up to 96% yield (eq. 2).

Comment: The characterization of Pd–NHC@MNP was performed by TEM, EDX, IR, TGA, DSC, ^1H NMR spectroscopy, and ETAAS analyses. In the Mizoroki–Heck reaction of butyl acrylate with iodobenzene, the catalyst was recovered magnetically and reused four times without loss of its catalytic activity (1st run: 85% yield, 3rd run: 87% yield, 5th run: 85% yield).

SYNFACTS Contributors: Yasuhiro Uozumi, Aya Tazawa
Synfacts 2015, 11(1), 0107
DOI: 10.1055/s-0034-1379723; **Reg-No.:** Y15014SF

Category

Polymer-Supported Synthesis

Key words

mesoporous copper(I) oxide

photocatalytic aza-Henry reaction

visible light

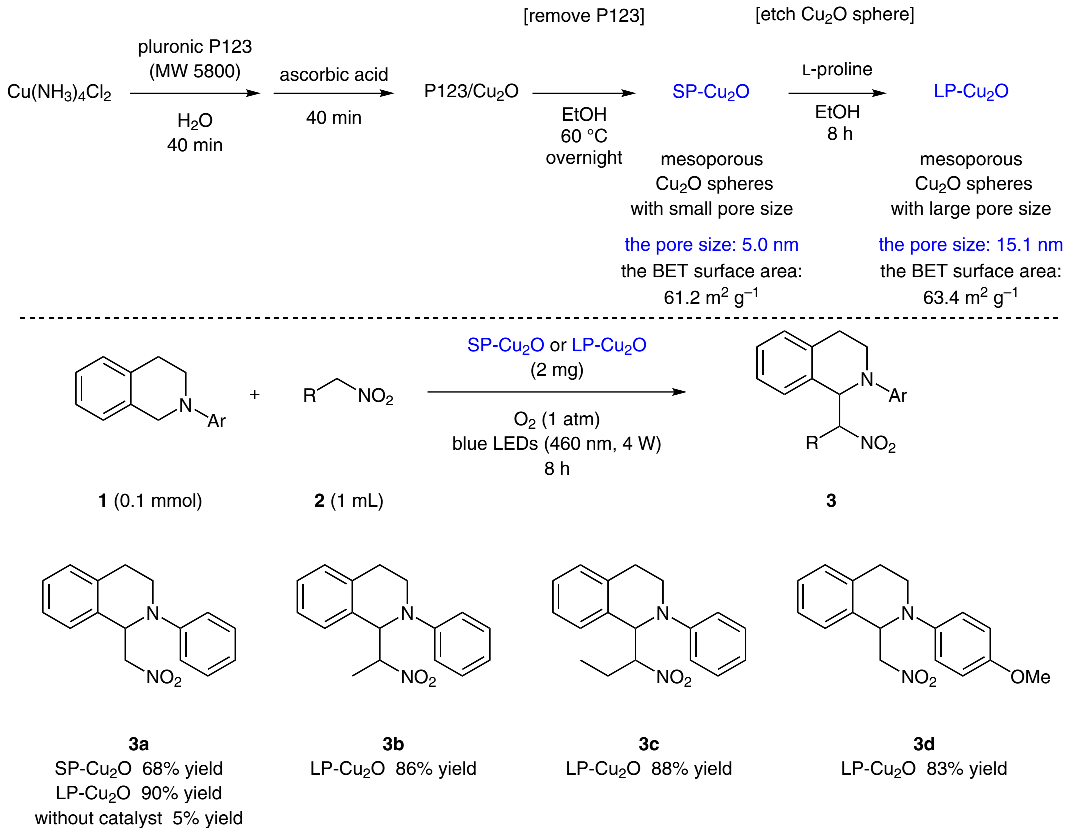
oxygen

J. WANG, J. MA, X. LI, Y. LI, G. ZHANG, F. ZHANG, X. FAN* (TIANJIN UNIVERSITY, P. R. OF CHINA)

Cu_2O Mesoporous Spheres with a High Internal Diffusion Capacity and Improved Catalytic Ability for the aza-Henry Reaction Driven by Visible Light

Chem. Commun. **2014**, *50*, 14237–14240.

Visible-Light-Promoted aza-Henry Reaction Using Mesoporous Cu_2O



Significance: Mesoporous copper(I) oxide spheres with different pore sizes (5 nm for SP-Cu_2O and 15 nm for LP-Cu_2O) were prepared and applied to the visible-light-promoted aza-Henry reaction. The reaction of *N*-aryl tetrahydroisoquinolines **1** with nitroalkanes **2** was carried out in the presence of LP-Cu_2O and molecular oxygen under the irradiation of blue LEDs to afford the corresponding coupling products **3** in 83–90% yield. The reaction without catalyst gave **3a** in only 5% yield under otherwise similar conditions.

Comment: The catalysts were characterized by SEM, TEM, XRD, and N_2 adsorption–desorption analyses. For the formation of **3a**, LP-Cu_2O was recovered by centrifugation and reused four times without significant loss of catalytic activity. SEM observation of LP-Cu_2O after the fifth run showed no change of its morphology. The preparation of mesoporous Cu_2O spheres with small pore size was previously reported by Shang, Zhang and Guo (*J. Mater. Chem*. **2012**, *22*, 856).

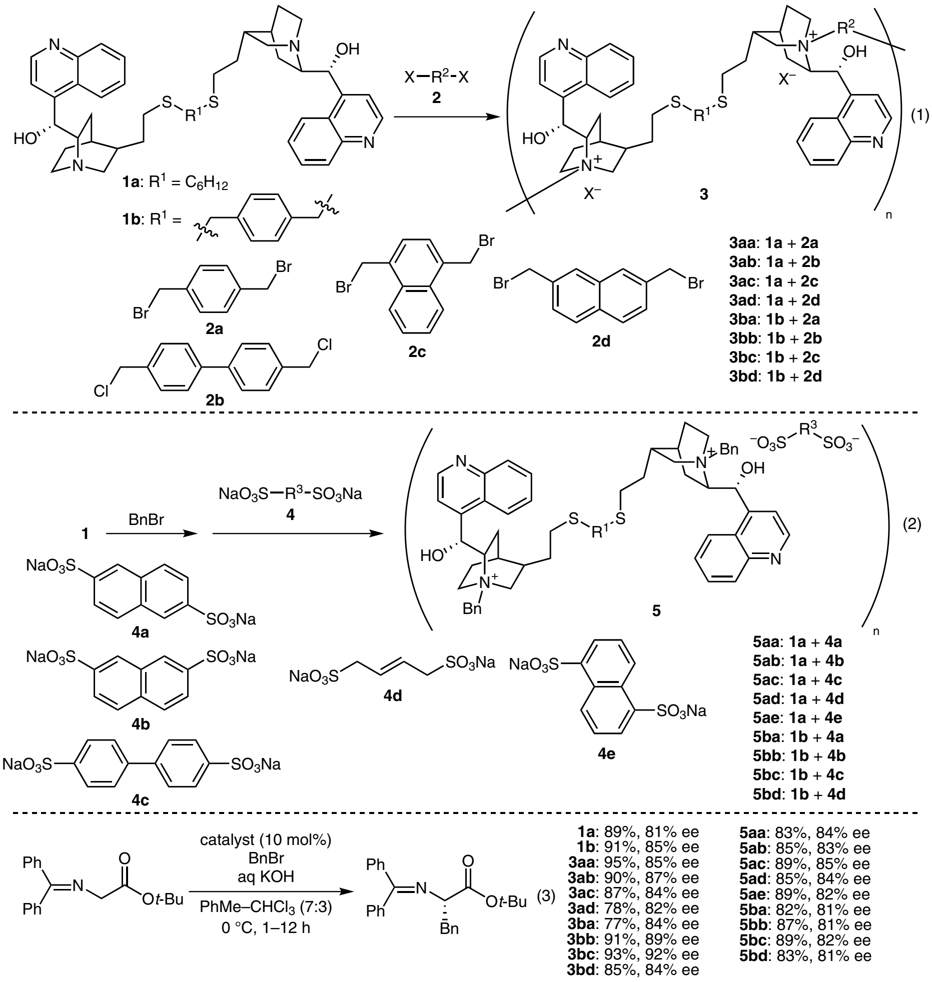
SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Aya Ohno
Synfacts 2015, 11(1), 0108 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379725; **Reg-No.:** Y15214SF

MD. R. ISLAM, P. AHAMED, N. HARAGUCHI, S. ITSUNO* (TOYOHASHI UNIVERSITY OF TECHNOLOGY, JAPAN)
Synthesis of Chiral Polymers Containing Thioetherified Cinchonidinium Repeating Units and Their Application to Asymmetric Catalysis
Tetrahedron: Asymmetry **2014**, *25*, 1309–1315.

Category
Polymer-Supported Synthesis

Key words
cinchonidium salts
chiral polymers
asymmetric α-benzylation

Asymmetric α-Benzylation with Cinchonidium Salt Based Polymers



Significance: Chiral polymers **3** and **5** were prepared from cinchonidine dimers **1** (eqs. 1 and 2). All polymers showed high catalytic performance in the asymmetric α-benzylation of *N*-diphenylmethylene glycine *tert*-butyl ester with benzyl bromide (eq. 3, 77–95% yield, 81–92% ee).

Comment: The polymer catalysts were recovered by filtration and reused without loss of catalytic performance. The reaction also took place at –40 °C to give the product with improved ee (with **3bc**: 24 h, 83% yield, 95% ee). The catalytic activity and the stereoselectivity observed with the polymeric catalysts **3** and **5** were comparable to those obtained with the homogeneous catalysts **1**.

SYNFACTS Contributors: Yasuhiro Uozumi, Makoto Nagaosa
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DOI: 10.1055/s-0034-1379724; **Reg-No.:** Y15114SF

Category

Polymer-Supported Synthesis

Key words

N-formylation

orthoformates

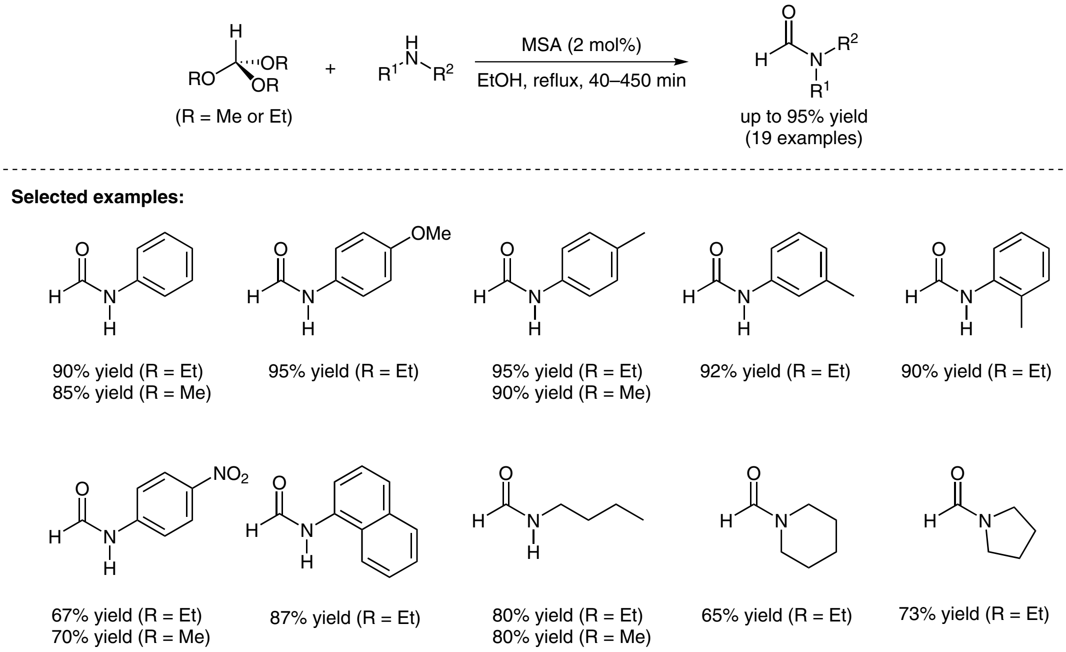
amines

molybdate sulfuric acid

B. KARAMI,* M. FARAHI, F. PAM (YASOUJ UNIVERSITY, IRAN)

A Green Protocol for the N-Formylation of Amines Using Molybdate Sulfuric Acid as a Reusable Solid Catalyst
Tetrahedron Lett. **2014**, *55*, 6292–6296.

N-Formylation of Amines Using Molybdate Sulfuric Acid



Significance: Molybdate sulfuric acid (MSA) catalyzed the N-formylation of amines with orthoformates to give the corresponding formamide derivatives in up to 95% yield (19 examples). In the N-formylation of aniline with triethyl orthoformate, the catalyst was recovered by filtration and reused three times with a slight loss of catalytic activity (1st reuse: 87% yield, 3rd reuse: 80% yield).

Comment: The catalytic activity of MSA was superior to that of the other catalysts (ZnO, $ZrOCl_2$, $MgBr_2$, $ZnCl_2$, and H_2SO_4).The authors have reported previously the preparation of molybdate sulfuric acid and its application to the synthesis of phenazines and quinoxalines (*Polycycl. Aromat. Compd.* **2011**, *31*, 97).

SYNFACTS Contributors: Yasuhiro Uozumi, Shuo Yan
Synfacts 2015, 11(1), 0110 Published online: 15.12.2014
DOI: 10.1055/s-0034-1379714; **Reg-No.:** Y14414SF